CLAIMS

WHAT IS CLAIMED IS:

1. A method of degrading a predetermined substrate comprising:

formulating a fluid or a solid device containing a degradable substrate and an inactivated substrate-degrading agent, said inactivated agent being responsive to a predetermined triggering signal ; and

applying a triggering signal to said fluid or solid device such that said agent becomes activated upon exposure to the triggering signal, the activated agent being capable of degrading the substrate under degradation promoting conditions.

2. The method of claim 1 further comprising encapsulating said degrading agent to provide an inactivated substrate-degrading agent.

3. The method of claim 2 wherein the step of applying a triggering signal comprises exposing the inactivated degrading agent to a stimulus selected from the group consisting of exposure to a reducing agents, oxidizers, chelating agents, radical initiators, carbonic acid, ozone, chlorine, bromine, peroxide, electric current, ultrasound, change in pH, change in salinity, change in ion concentration, change in temperature and change in pressure, said inactivated degrading agent being capable of physically and/or chemically responding to said stimulus.

4. The method of claim 1 wherein said step of applying a triggering signal comprises exposing the inactivated degrading agent to a change in pH.

5. The method of claim 4 wherein said step of exposing the inactivated degrading agent to a change in pH comprises establishing an acid pH environment.

6. The method of claim 5 wherein said step of establishing an acid pH environment comprises exposing the inactivated degrading agent to carbonic acid.

7. The method of claim 1 wherein said step of applying a triggering signal comprises

exposing the inactivated degrading agent to a change in salinity.

8. The method of claim 1 wherein said step of applying a triggering signal comprises exposing the inactivated degrading agent to a reducing agent.

9. The method of claim 1 wherein said step of applying a triggering signal comprises exposing the inactivated degrading agent to an oxidizer.

10. The method of claim 1 wherein said step of applying a triggering signal comprises exposing the inactivated degrading agent to a chelating agent.

11. The method of claim 1 wherein said step of applying a triggering signal comprises exposing the inactivated degrading agent to a radical initiator.

12. The method of claim 1 wherein said step of applying a triggering signal comprises exposing the inactivated degrading agent to ozone.

13. The method of claim 1 wherein said step of applying a triggering signal comprises exposing the inactivated degrading agent to chlorine or bromine.

14. The method of claim 1 wherein said step of applying a triggering signal comprises exposing the inactivated degrading agent to peroxide.

15. The method of claim 1 wherein said step of applying a triggering signal comprises exposing the inactivated degrading agent to an electric current.

16. The method of claim 1 wherein said step of applying a triggering signal comprises exposing the inactivated degrading agent to ultrasound.

17. The method of claim 1 wherein said step of applying a triggering signal comprises exposing the inactivated degrading agent to a change in ion concentration.

18. The method of claim 1 wherein said step of applying a triggering signal comprises exposing the inactivated degrading agent to a change in temperature.

19. The method of claim 1 wherein said step of applying a triggering signal comprises exposing the inactivated degrading agent to a change in pressure.

20. The method of claim 1 wherein said degrading agent comprises at least one enzyme having activity for degrading said substrate under degradation promoting conditions.

21. The method of claim 20 further comprising encapsulating said at least one enzyme with an encapsulating material that is responsive to said triggering signal such that at least a portion of said enzyme is released by said encapsulating material upon exposure to a triggering signal.

22. The method of claim 21 wherein said encapsulating material is formed of a co-polymer of (a) an ethylenically unsaturated hydrophobic monomer with (b) a free base monomer of the formula

$$CH_2 = CR^1COXR^2NR^3R^4$$

where R is hydrogen or methyl, R^2 is alkylene containing at least two carbon atoms, X is O or NH, R^3 is a hydrocarbon group containing at least 4 carbon atoms and R^4 is hydrogen or a hydrocarbon group.

23. The method of claim 22 wherein R^3 is t-butyl and R^4 is hydrogen.

24. The method of claim 22 wherein R^1 is methyl, R2 is ethylene and X is O.

25. The method of claim 22 wherein the hydrophobic monomer is a styrene or methylmethacrylate.

26. The method of claim 22 wherein said encapsulating material is a co-polymer of styrene or methyl methacrylate with t-butyl amino ethyl methacrylate.

27. The method of claim 22 wherein said co-polymer is 55 to 80 weight% styrene, methyl styrene or methyl methacrylate with 20 to 45 weight% t-butylamino-ethyl methacrylate.

28. The method of claim 21 further comprising maintaining enzymatic activity promoting conditions.

29. The method of claim 21 further comprising establishing enzymatic activity inhibiting conditions.

30. The method of claim 21 wherein the fluid or solid device comprises at least two inactivated enzymes, wherein the inactivated enzymes are capable of being reactivated by the same or different triggering signals, such that upon reactivation the reactivated enzymes are capable of acting upon the same or different substrates independently or in concert.

31. The method of claim 21 wherein said at least one enzyme comprises an endo-amylase.

32. The method of claim 31 wherein said at least one enzyme comprises alpha-amylase.

33. The method of claim 21 wherein the enzyme is selected from the group consisting of exo-amylases, isoamylases, glucosidases, amylo-glucosidases, malto-hydrolases, maltosidases, isomalto-hydrolases and malto-hexaosidases.

34. The method of claim 21 wherein the reactivated enzyme is capable of being inactivated by application of a second triggering signal, wherein the second triggering signal may be the same or a different triggering signal, such that the inactivated enzyme no longer acts on the substrate.

35. The method of claim 1 wherein the degradable substrate is selected from the group consisting of celluloses, derivatized celluloses, starches, derivatized starches, xanthans and derivatized xanthans.

36. The method of claim 1 wherein the fluid is chosen from the group consisting of circulating drilling fluid, completion fluid, stimulation fluid and workover fluid.

37. The method of claim 1 wherein the fluid is a fracturing fluid.

38. The method of claim 1 wherein said solid device comprises a self-destructing bridging particle containing a degradable substrate and an activatable inactivated enzyme for reversible fluid loss control.

39. The method of claim 1 wherein said solid device comprises at least one degradable polymer and an activatable inactivated enzyme fashioned into hardware for use downhole or on the surface.

40. A method of increasing the flow of hydrocarbons from a well, the method comprising:

formulating a fluid comprising a degradable polymeric substrate and an inactivated enzyme;

introducing the fluid into a downhole environment; and,

applying a triggering signal to the fluid, the triggering signal being sufficient to reactivate the inactivated enzyme to give a reactivated enzyme,

the reactivated enzyme being capable of selectively degrading the substrate sufficient to alter a physical property of the fluid such that the flow of hydrocarbons is increased.

41. The method of claim 40 wherein the step of introducing the fluid into a downhole environment comprises forming a filter cake containing said degradable substrate and said inactivated enzyme.

42. The method of claim 40 wherein the fluid comprises more than one inactivated enzyme, wherein the inactivated enzymes are capable of being activated by the same or different triggering signals, wherein upon activation the activated enzymes are capable of acting upon the same or different substrates.

43. The method of claim 40 wherein the fluid is chosen from the group consisting of a circulating drilling fluid, a completion fluid, a workover fluid and a stimulation fluid.

44. A method of degrading filter cake, the method comprising:

formulating a fluid comprising a polymeric viscosifier or fluid loss control agent and an inactivated enzyme;

introducing the fluid into a downhole environment such that a filter cake containing said polymeric viscosifier or fluid loss control agent and said inactivated enzyme is formed;

applying a triggering signal to the fluid, the triggering signal being sufficient to reactivate the inactivated enzyme to give a reactivated enzyme,

the reactivated enzyme being capable of selectively degrading said polymeric viscosifier or fluid loss control agent such that said filter cake containing said viscosifier at least partially disintegrates.

45. The method of claim 44 further comprising dislodging a piece of drilling equipment from said at least partially disintegrated filter cake.

46. A method of degrading a contaminant arising from a subterranean formation comprising:

formulating a fluid comprising an inactivated substrate-degrading agent;

introducing the fluid into a downhole environment that may contain a predetermined contaminant that is a substrate capable of being degraded by the agent under degradation promoting conditions; and

applying a triggering signal to the fluid, either by direct action or by the action of the contaminant, the triggering signal being sufficient to reactivate the inactivated agent to give a reactivated agent,

allowing the reactivated substrate-degrading agent to degrade the contaminant.

47. The method of claim 46 wherein the fluid is a circulating drilling fluid, completion fluid or workover fluid.

48. The method of claim 46 wherein the contaminant is H_2S.

49. A wellbore treatment method comprising:

formulating a fluid or a solid device containing an inactivated substrate-degrading agent, said inactivated agent being responsive to a predetermined triggering signal such that said agent becomes activated upon exposure to the triggering signal, the activated agent being capable of degrading the substrate under degradation promoting conditions;

introducing the fluid into a downhole environment containing a predetermined substrate capable of being degraded by the agent under degradation promoting conditions; and

providing the trigger to activate the substrate-degrading agent; and

allowing the substrate-degrading agent to degrade the substrate.

50. A composition for use in hydrocarbon exploitation operations, the composition comprising a fluid or a solid device containing:

at least one degradable substrate; and

an encapsulated substrate-degrading agent, said encapsulated agent being capable of responding to a triggering signal such that said agent becomes sufficiently unencapsulated to allow said agent to degrade said substrate under degradation promoting conditions such that a physical or chemical property of the substrate is altered.

51. The composition of claim 50 wherein the encapsulated substrate-degrading agent is inactivated by encapsulation with a material that is capable of responding to the triggering signal by making the degrading agent available to the degradable substrate.

52. The composition of claim 50 wherein said triggering signal comprises a change in pH of a medium contacting said encapsulated agent.

53. The composition of claim 50 wherein said triggering signal comprises exposing the inactivated degrading agent to a change in pH.

54. The composition of claim 50 wherein said triggering signal comprises a change to a predetermined acid pH.

55. The composition of claim 50 wherein said triggering signal comprises exposure of said encapsulated agent to carbonic acid.

56. The composition of claim 50 wherein said triggering signal comprises exposure of said encapsulated agent to a change in salinity.

57. The composition of claim 50 wherein said triggering signal comprises exposure of said encapsulated agent to a reducing agent.

58. The composition of claim 50 wherein said triggering signal comprises exposure of said encapsulated agent to an oxidizer.

59. The composition of claim 50 wherein said triggering signal comprises exposure of said encapsulated agent to a chelating agent.

60. The composition of claim 50 wherein said triggering signal comprises exposure of said encapsulated agent to a radical initiator.

61. The composition of claim 50 wherein said triggering signal comprises exposure of said encapsulated agent to ozone.

62. The composition of claim 50 wherein said triggering signal comprises exposure of said encapsulated agent to chlorine or bromine.

63. The composition of claim 50 wherein said triggering signal comprises exposure of said encapsulated agent to peroxide.

64. The composition of claim 50 wherein said triggering signal comprises exposure of said encapsulated agent to an electric current.

65. The composition of claim 50 wherein said triggering signal comprises exposure of said encapsulated agent to ultrasound.

66. The composition of claim 50 wherein said triggering signal comprises exposure of said encapsulated agent to a change in ion concentration.

67. The composition of claim 50 wherein said triggering signal comprises exposure of said encapsulated agent to a change in temperature.

68. The composition of claim 50 wherein said triggering signal comprises exposure of said encapsulated agent to a change in pressure.

69. The composition of claim 50 wherein the substrate degrading agent comprises at least one inactivated enzyme, wherein the inactivated enzymes are capable of being activated by the same or different triggering signals, wherein upon activation the reactivated enzymes are capable of acting upon the same or different substrates.

70. The composition of claim 50 wherein the composition is chosen from the group consisting of a circulating drilling fluid, a completion fluid, a stimulation fluid, a workover fluid, a bridging particle and a solid/hardware device.

71. The composition of claim 50 wherein the substrate is selected from the group consisting of celluloses and derivatized celluloses.

72. The composition of claim 50 wherein the substrate is selected from the group consisting of starches and derivatized starches

73. The composition of claim 50 wherein the substrate is selected from the group consisting of xanthans and derivatized xanthans.

74. The composition of claim 50 wherein said at least one degradable substrate contributes to the structural integrity of said device or to the structural integrity of a residue of said fluid such

that degradation of said at least one substrate causes a physical change in said composition.

75. The composition of claim 50 wherein said substrate-degrading agent comprises at least one enzyme.

76. The composition of claim 75 wherein said at least one enzyme comprises an endo-amylase.

77. The composition of claim 75 wherein said at least one enzyme comprises alpha-amylase.

78. The composition of claim 75 wherein at least one enzyme is selected from the group consisting of exo-amylases, isoamylases, glucosidases, amylo-glucosidases, malto-hydrolases, maltosidases, isomalto-hydrolases and malto-hexaosidases.

79. The composition of claim 50 wherein said encapsulated agent comprises an encapsulation material formed of a co-polymer of (a) an ethylenically unsaturated hydrophobic monomer with (b) a free base monomer of the formula

$$CH_2 = CR^1COXR^2NR^3R^4$$

where R is hydrogen or methyl, R^2 is alkylene containing at least two carbon atoms, X is O or NH, R^3 is a hydrocarbon group containing at least 4 carbon atoms and R^4 is hydrogen or a hydrocarbon group.

80. The composition of claim 79 wherein said encapsulating material is a co-polymer of styrene or methyl methacrylate with t-butyl amino ethyl methacrylate.

81. The composition of claim 79 wherein R^3 is t-butyl and R^4 is hydrogen.

82. The composition of claim 79 wherein R^1 is methyl, R2 is ethylene and X is O.

83. The composition of claim 79 wherein the hydrophobic monomer is a styrene or methylmethacrylate.

84. The composition of claim 79 wherein said encapsulation material is a co-polymer of styrene or methyl methacrylate with t-butyl amino ethyl methacrylate.

85. The composition of claim 84 wherein said co-polymer is 55 to 80 weight% styrene, methyl styrene or methyl methacrylate with 20 to 45 weight% t-butylamino-ethyl methacrylate.